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FOR

**APPARATUS AND METHOD FOR
EXPOSING A SUBSTRATE TO PLASMA RADICALS**

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APPARATUS AND METHOD FOR
EXPOSING A SUBSTRATE TO PLASMA RADICALS

BACKGROUND OF THE INVENTION

Field of the Invention

The invention relates to the field of wafer or substrate plasma reactions and more specifically to an apparatus and method for exposing a wafer or substrate to a plasma of predominantly plasma radicals.

Description of Related Art

In the fabrication of modern integrated circuits, such as microprocessors and memories, oxidation processes are used to passivate or oxidize semiconductor films. Popular methods to oxidize silicon surfaces and films such as, for example, polysilicon gate electrodes and substrates include pure oxygen (O_2) and water vapor or steam (H_2O) oxidation processes. In either case, the oxygen or water vapor is brought into a chamber to react with the silicon-containing surfaces to form silicon dioxide (SiO_2).

In many oxidation processes for ultra-high performance integrated circuit applications, a pure SiO_2 film may not be desirable as the final structure. For example, although an SiO_2 film may provide adequate insulative properties, thin SiO_2 films have been found to be penetrable by dopants leading to undesirable results. For example, in complementary metal oxide semiconductor (CMOS) circuits, gate doping is utilized, in part, to lower the threshold voltage (V_T) associated with an individual transistor device. Thus, for example, a polysilicon gate will be doped with boron as part of a PMOS device or phosphorous, arsenic, or antimony as part of an NMOS

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device. As the gate oxide beneath the polysilicon gate gets smaller, for example in the range of 0.10-0.20 microns or less, dopants implanted into the gate, particularly boron, diffuse or migrate through the gate oxide, particularly during a high temperature annealing activation step conventionally performed to activate the dopants in the diffusion or junction regions. In the case of boron in the gate, some of the boron diffuses through the gate oxide and gets deposited in the channel beneath the gate oxide adding more charge to the channel. The additional charge becomes scattering centers to charge carriers conducting the current. The scattering creates electric field changes that degrade the mobility of the device. The diffusion of the boron into the channel also unacceptably modifies the V_T away from the predicted value for a device.

To prevent dopants from diffusing through thin oxides, such as boron through a thin gate oxide, prior art processes have incorporated nitrogen-containing sources such as nitrous oxide (N_2O), nitrogen oxide (NO), and ammonia (NH_3). The nitrogen-containing material forms a film or layer (typically a silicon nitride (Si_3N_4) or a silicon oxynitride ($Si_xN_yO_z$) film or layer) that acts as a barrier layer to prevent the diffusion of dopants through the oxide.

In the case of gate oxides, some prior art methods place nitrogen-containing materials or films at the gate oxide/substrate interface. A prior art NO growth and anneal method, for example, typically results in a high nitrogen incorporation (up to nine percent) at a gate oxide/silicon substrate interface. The nitrogen acts as an excellent diffusion barrier, but the nitrogen present in such high percentage at the interface degrades channel mobility. Other

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prior art methods contaminate the oxide or do not provide a significant penetration barrier to dopants. For example, an NH_3 anneal forms a good barrier layer to diffusing dopants, but the reliability of the device is degraded due to hydrogen incorporation. A prior art N_2O growth or anneal method incorporates less than three percent nitrogen at the substrate interface, but does not provide a good enough penetration barrier for thin gate oxides.

What is needed is a method and apparatus for incorporating a barrier material on an oxide that may be accomplished in a thermally efficient manner and that does not degrade device performance.

SUMMARY

An apparatus and method for exposing a substrate to plasma radicals is disclosed. In one embodiment of the apparatus, a first reaction chamber is adapted to generate a plasma from a process gas. In general, the plasma generated consists primarily of charged ions, radicals, and electrons. A second reaction chamber coupled to the first reaction chamber is adapted to house a substrate at a location inside the second reaction chamber. The substrate may have one or more layers of a material or materials on a surface, such as an oxide layer or layers. The second reaction chamber is coupled to the first reaction chamber such that the plasma traveling from the first reaction chamber to the second reaction chamber is separated from the substrate by a distance equivalent to the lifetime of the ions at a given plasma discharge rate. In this manner, radicals reach the substrate and react with the substrate while the ions that were initially also present in the plasma become charge neutral.

In the example of a nitridation reaction in which nitrogen plasma is incorporated into an oxide on the substrate, the nitrogen radicals of a nitrogen plasma rapidly react with the oxide to incorporate nitrogen into the exposed surface of the oxide. In terms of barrier layer protection to a gate oxide, the nitrogen is incorporated primarily in the exposed surface of the oxide and not at the gate oxide/substrate interface. In this manner, the presence of an adequate amount of nitrogen to act as a barrier layer, disposed away from the substrate interface, will reduce the scattering centers caused by otherwise penetrable dopants without deleterious effects on channel mobility.

One embodiment of the method of the invention involves generating a plasma comprising ions and radicals in a first chamber, placing a substrate in a second chamber, and transferring the radicals into the second chamber to react with or be incorporated into the substrate. In the case of a nitrogen plasma, for example, the method uses a nitrogen plasma to create nitrogen radicals that can be used to incorporate nitrogen into an oxide such as, for example, to act as a barrier layer as described above. The method is useful to incorporate nitrogen into gate oxides and create barrier layers to penetrable gate dopants because, in one embodiment, the incorporated nitrogen does not migrate to the gate oxide/substrate interface. The barrier layer may therefore be created without the deleterious effects on gate performance associated with prior art methods, such as channel mobility degradation.

Additional features and benefits of the invention will become apparent from the detailed description, figures, and claims set forth below.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a cross-sectional schematic illustration of a semiconductor substrate having an oxide layer undergoing a nitridation by radicals of a plasma in accordance with an embodiment of the invention.

Figure 2 shows the substrate of **Figure 1** after the processing step of forming a nitride film on or in the surface of the oxide layer in accordance with an embodiment of the invention.

Figure 3 is a schematic illustration of a remote plasma system in accordance with an embodiment of the invention including a system controller, a rapid thermal heating apparatus containing a wafer, a plasma applicator and a microwave source.

Figure 4 is a schematic illustration of a plasma applicator for use in supplying radicals of a plasma to a reaction chamber in accordance with an embodiment of the invention.

Figure 5 is an illustrative block diagram of the hierarchical control structure of the control signal generation logic to operate the process system according to an embodiment of the invention.

Figure 6 is a flowchart that illustrates a remote plasma nitridation process in accordance with an embodiment of the invention.

Figure 7 is a Secondary Ion Mass Spectroscopy (SIMS) profile of a silicon substrate containing a dielectric layer formed by the nitridation of an oxide by a remote plasma source under a first set of reaction conditions in accordance with an embodiment of the invention.

Figure 8 is a schematic illustration of a dielectric layer overlying a silicon substrate, the dielectric layer formed by the plasma nitridation of an SiO_2 layer on a substrate according to a first set of reaction conditions.

Figure 9 is a Secondary Ion Mass Spectroscopy (SIMS) profile of a silicon substrate containing a dielectric layer formed by the nitridation of an oxide by a remote plasma source under a second set of reaction conditions in accordance with an embodiment of the invention.

Figure 10 is a schematic illustration of a dielectric layer overlying a silicon substrate, the dielectric layer formed by the plasma nitridation of an SiO_2 layer on a substrate according a second set of reaction conditions.

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DETAILED DESCRIPTION

The invention describes an apparatus and method for incorporating a plasma into a substrate or a material on a substrate using a remote plasma source. In general, plasma sources generated by, for example, an energetic excitation of gaseous molecules consist of a plasma of charged ions, radicals, and electrons. The invention recognizes that radicals of a plasma react in a much more desirable manner with a substrate or a material on a substrate, such as an oxide, than ions or a mixture of radicals and ions. In that regard, the invention describes the plasma source as remote to provide an apparatus and a method of eliminating the majority of the ions of the plasma such that preferably only the radicals of the plasma react with a substrate or material on a substrate.

In the following description, numerous specific details such as apparatus configurations as well as process specifics such as time and temperature are set forth in order to provide a thorough understanding of the invention. One skilled in the art will appreciate the ability to use alternative configurations and process details to the disclosed specifics without departing from the invention. In other instances, well known semiconductor processing equipment and techniques have not been described in detail in order to not unnecessarily obscure the invention.

Figures 1 and **2** illustrate an embodiment of the method of the invention. **Figure 1** shows layer 110, such as for example, silicon dioxide (SiO_2) layer 110 overlying substrate 100. In one embodiment, SiO_2 layer 110 will serve as a gate oxide to insulate a transistor gate from the substrate. Substrate 100 is, for example, a silicon substrate 100. In **Figure 1**, SiO_2

layer 110 is bombarded by plasma 115. The reactive portion of plasma 115 is comprised substantially of radicals. The invention contemplates that substantially all ions present in the plasma at the plasma generation (with the radicals) are eliminated prior to coming in contact with SiO_2 layer 110. One way positively charged ions are eliminated is by combining with electrons (also present in the plasma at the plasma generation) to return to a non-ionic or charge neutral state. A plasma may be substantially free of the majority of the ions by separating the plasma generation source from the substrate location, e.g., the reaction site, by a distance longer than the lifetime of the ions at a given plasma discharge rate. In this manner, the radicals survive the travel distance to substrate 100, but ions do not, but instead lose their ionic character and become charge neutral.

In one embodiment, SiO_2 layer 110 is a gate oxide and the plasma is a nitrogen plasma incorporating nitrogen into the gate oxide to act as a barrier layer. **Figure 2** shows substrate 100 after the reaction between the radicals of the plasma and SiO_2 layer 110. **Figure 2** schematically illustrates the formation of, for example, a nitrogen-containing material or layer 120 overlying SiO_2 layer 110. A nitrogen plasma of nitrogen radicals (N^*) reacts primarily with the oxide or displaces oxygen at the surface of SiO_2 layer 110 to yield a dielectric layer (i.e., SiO_2 layer 110 plus nitrogen-containing material or layer 120) having a significantly greater concentration of nitrogen-containing material at the surface of the dielectric layer as opposed to interface 105 between the dielectric layer and substrate 100. In this manner, the presence of nitrogen-containing material in the dielectric acts as an effective barrier layer to prevent the penetration

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of dopants, such as boron, through SiO_2 layer 110. Since the nitrogen-containing material or layer 120 is not present in significant amounts at interface 105, the negative effects on device performance seen in prior art structures should not be encountered.

It is to be appreciated that the invention is not limited to a process that results in a strict placement of a film or layer at the reaction surface, i.e., that the plasma reaction takes place in such a way to produce distinct layers of plasma-containing material and oxide. Instead, as will be discussed in detail below, in certain embodiments, the radicals of the plasma react and interact, for example, within the oxide during the exposure of the radicals to the reaction surface. In the case of a nitridation of a gate oxide, for example, the nitrogen-containing material is produced effectively in or on SiO_2 layer 110 by exposing SiO_2 layer 110 to a plasma of predominantly N^* radicals. One theory is that N^* radicals displace oxygen atoms in SiO_2 layer 110 to form Si_3N_4 and $Si_xO_yN_z$ material.

Figure 3 illustrates one embodiment of an apparatus or system used to react a plasma of predominantly radicals of a plasma with a substrate such as substrate 100 containing a material layer such as SiO_2 layer 110. The apparatus or system includes a rapid thermal processing (RTP) apparatus 200, such as but not limited to, the Applied Materials, Inc. RTP Centura™ with a Honeycombed Source. Another suitable RTP apparatus and its method of operation are set forth in U.S. Patent No. 5,155,336, assigned to the assignee of the invention. Other types of thermal reactors may be substituted for the RTP apparatus such as, for example, the Epi or Poly

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Centur™ Single Wafer "Cold Wall" Reactor by Applied Materials, Inc., used to form high temperature films such as epitaxial silicon, polysilicon, oxides, and nitrides. The DielectricxZ™ chamber by Applied Materials is also suitable.

Coupled to RTP apparatus 200 is plasma applicator 300 to provide radicals of a plasma to RTP apparatus 200. Coupled to plasma applicator 300 is energy source 450 to generate an excitation energy to create a plasma.

In the embodiment illustrated in **Figure 3,** RTP apparatus 200 includes a process chamber 213 enclosed by side wall 214 and bottom wall 215. Side wall 214 and bottom wall 215 are preferably made of stainless steel. The upper portion of side wall 214 of chamber 213 is sealed to window assembly 217 by "O" rings. Radiant energy light pipe assembly 218 is positioned over and coupled to window assembly 217. Light pipe assembly 218 includes a plurality of tungsten halogen lamps 219, for example, Sylvania EYT lamps, each mounted into light pipes 221 that can be stainless steel, brass, aluminum, or other metal.

Wafer or substrate 100 is supported on an edge inside chamber 213 by support ring 262 typically made of silicon carbide. Support ring 262 is mounted on a rotatable quartz cylinder 263. By rotating quartz cylinder 263, support ring 262 and wafer or substrate 100 are caused to rotate. An additional silicon carbide adapter ring can be used to allow wafers or substrates of different diameters to be processed (e.g., 150 millimeters as well as 200 millimeters). The outside edge of support ring 262 preferably extends less than two inches from the outside diameter of wafer or substrate 100. The volume of chamber 213 is approximately two liters.

Bottom wall 215 of RTP apparatus 200 includes a gold-coated top surface 211 for reflecting energy onto the back side of wafer or substrate 100. Additionally, RTP apparatus 200 includes a plurality of fiber optic probes positioned through bottom wall 215 of RTP apparatus 200 to detect the temperature of wafer or substrate 100 at a plurality of locations across its bottom surface.

RTP apparatus 200 includes gas inlet 269 formed through side wall 214 for injecting process gas or radicals of a plasma into chamber 213 to allow various processing steps to be carried out in chamber 213. Coupled to gas inlet 269 is plasma applicator 300 to inject radicals of a plasma into chamber 213. Positioned on the opposite side of gas inlet 269, in side wall 214, is gas outlet 270. Gas outlet 270 is coupled to a vacuum source, such as a pump, to exhaust process gas from chamber 213 and to reduce the pressure in chamber 213. The vacuum source maintains the desired pressure while process gas, including radicals of a plasma, is continually fed into chamber 213 during processing.

Light pipe assembly 218 preferably includes 187 lamps 219 positioned in a hexagonal array or in a "honeycombed" shape. Lamps 219 are positioned to adequately cover the entire surface area of wafer or substrate 100 and support ring 262. Lamps 219 are grouped in zones that can be independently controlled to provide for extremely uniform heating of wafer or substrate 100. Light pipes 221 can be cooled by flowing a coolant, such as water, between the various heat pipes.

Window assembly 217 includes a plurality of short light pipes 241 that are brazed to upper/lower flange plates that have their outer edges sealed to outer wall 244. A coolant, such as water, can be injected into the space between light

pipes 241 to serve to cool light pipes 241 and flanges. Light pipes 241 register with light pipes 221 of the illuminator. The water-cooled flange with the light pipe pattern that registers with the lamp housing is sandwiched between two quartz plates 247 and 248. These plates are sealed to the flange with "O" rings near the periphery of the flange. Quartz plates 247 and 248 include grooves that provide communication between the plurality of light pipes 241. A vacuum can be produced in the plurality of light pipes 241 by pumping through tube 253 connected to one of the light pipes 241 which is in turn connected to the rest of the pipe by a very small recess or groove in the face of the flange. Thus, when the sandwiched structure is placed on chamber 213, the metal flange (typically stainless steel and of excellent mechanical strength) provides adequate structural support. Lower quartz plate 248--the one actually sealing chamber 213-- experiences little or no pressure differential because of the vacuum on each side and thus can be made very thin. The adaptor plate concept of window assembly 217 allows quartz plates to be easily changed for cleaning or analysis. In addition, the vacuum between quartz plates 247 and 248 of window assembly 217 provides an extra level of protection against toxic gases escaping from the reaction chamber.

RTP apparatus 200 is a single wafer reaction chamber capable of ramping the temperature of wafer or substrate 100 at a rate of 25-100°C/second. RTP apparatus 200 is said to be a "cold wall" reaction chamber because the temperature of wafer or substrate 100 during, for example, an oxidation process is at least 400°C greater than the temperature of chamber side wall 214. Heating/cooling fluid can be

circulated through side walls 214 and/or bottom wall 215 to maintain the walls at a desired temperature.

As noted above, plasma applicator 300 is coupled to RTP apparatus 200 to provide a source of radicals of a plasma to RTP apparatus 200. In one embodiment, plasma applicator 300 is connected to RTP apparatus 200 by inlet pipe 360. Plasma applicator 300 also includes gas inlet 310. Coupled to gas inlet 310 is a source gas, such as a tank of nitrogen-containing gas, including, but not limited to, N_2 gas. Plasma applicator 300 also includes a tube 311 to couple plasma applicator 300 through a wave guide to energy source 450.

Figure 3 illustrates an embodiment wherein plasma applicator 300 is remote from RTP apparatus 200 in that the plasma is generated outside chamber 213 of RTP apparatus 200. By locating plasma applicator 300 remotely from chamber 213 of RTP apparatus 200, a plasma source can be selectively generated to limit the composition of the plasma exposed to wafer or substrate 100 to predominantly radicals. Thus, a plasma of ions, radicals, and electrons is generated in plasma applicator 300. However, because of the size (e.g., length and volume) of plasma applicator 300 or the combined size of plasma applicator 300 and inlet pipe 360, all or the majority of ions generated by the excitation of the process gas to a plasma outlive their ionic lifetime and become charge neutral. Thus, the composition of the plasma that is supplied to gas inlet 269 of RTP apparatus 200 is predominantly radicals.

In the case of a nitrogen source gas, for example, excitation by microwave radiation produces a plasma of N^* radicals, positively charged ions such as N^+ and N^{2+} ions, and electrons. The N^* radicals are believed to be neutral atoms

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occupying a high energy state. The apparatus of the invention is configured such that the positively charged ions (e.g., N^+ and N^{2+} ions) become charge neutral either in plasma applicator 300 or inlet pipe 360 and thus generally do not reach chamber 213 of RTP apparatus 200. Positively charged nitrogen ions become charge neutral by combining with available electrons to lose their ionic state. In this manner, predominantly N^* radicals and charge neutral nitrogen reach chamber 213 and are exposed to wafer or substrate 100 or a material on wafer or substrate 100 (e.g., an oxide layer). By combining with positively charged nitrogen ions, electrons produced in the plasma are not, in general, exposed to substrate 100 in chamber 213. Thus, charged particles of the plasma are not available to sputter substrate 100 or SiO_2 layer 110 on substrate 100. In this manner, the reaction of a nitrogen plasma of N^* radicals, results in a relatively damage-free dielectric layer.

Figure 4 illustrates an embodiment of plasma applicator 300 that is useful in the remote plasma generation apparatus of the invention. Plasma applicator 300 is particularly useful in generating a nitrogen plasma according to the nitridation reaction described above with reference to **Figures 1** and **2** and the accompanying text. Plasma applicator 300 includes body 305 of, for example, aluminum or stainless steel. Body 305 surrounds tube 320. Tube 320 is, for example, quartz or sapphire. Tube 320 preferably does not have any electrical bias present that might attract charged particles, e.g., ions. One end of body 305 includes gas inlet 310. Coupled to gas inlet 310 is source gas 313, such as a tank of nitrogen-containing gas including, but not limited to,

N$_2$ gas. Flow controller 426, such as a mass flow controller, is coupled between source gas 313 and gas inlet 310 to regulate the flow of gas to plasma applicator 300. Flow controller 426 receives, in one embodiment, an analog signal from system controller 260 (such as, for example, a signal between 0 and 5 volts) that actuates a value to control the flow rate or amount of gas released from source gas 313 to gas inlet 310. Conversion board 272 is placed, in this embodiment, between flow controller 426 to coordinate the signals between system controller 260 and flow controller 426, in the instance where, for example, the signals are scaled differently. The diameter of the opening of gas inlet 310 is selected to allow a desired flow rate of source gas 313 into tube 320.

Positioned on the opposite side of gas inlet 310 is radicals outlet 375. Radicals outlet 375 is coupled to inlet pipe 360 to supply, in one embodiment, radicals of a plasma to chamber 213 of RTP apparatus 200. Radicals outlet 375 typically has a diameter larger than gas inlet 310 to allow the excited radicals to be efficiently discharged at the desired flow rate and to minimize the contact between the radicals and tube 320. The flow rate of the radicals generated and discharged by plasma applicator 300 is determined primarily by the source gas inlet flow, the dimensions of tube 320 and radicals outlet 375, and the pressure in plasma applicator 300.

At a position between gas inlet 310 and radicals outlet 375 of body 305 is energy source inlet 380. Energy source inlet 380 allows the introduction into tube 320 of excitation energy, such as an energy having a microwave frequency, from energy source 450. In the case of a microwave frequency, the

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excitation energy moves into body 305 of plasma applicator 300 and through tube 320 to excite the gas source traveling in a direction perpendicular to energy source inlet 380 into a plasma. The excitation energy does this by disrupting the otherwise stable configuration of some of the gas molecules into excited or higher energy states such as certain radicals and ions. In the case of N_2, for example, the microwave excitation in plasma applicator 300 produces N^* radicals, positively charged ions such as N^+ and N^{2+}, and electrons.

One goal of the system and method of the invention is to minimize the reaction of ions of a plasma (e.g., N^+ and N^{2+} ions) with substrate 100 or the oxide overlying the surface of substrate 100. Thus, in one embodiment, tube 320 of plasma applicator 300 is constructed of a length such that, for a given flow rate of a processed gas (e.g., a given plasma generation rate), substantially all ions created by the excitation by the energy source are extinguished or reacted with electrons or other charged particles to lose their excited state prior to exiting tube 320. In one embodiment, a plasma of predominantly radicals is delivered to substrate 100 in chamber 213. It is to be appreciated that in some instances, a small amount of ions of a plasma may be delivered to the substrate site without significant effect on the reaction between the radicals and the substrate or the radicals and material on the substrate. The invention recognizes that radicals tend to react in a much more desirable manner than ions or a mixture of radicals and ions. Accordingly, the invention seeks, in one aspect, to minimize the exposure of the substrate or the material on the substrate to ions.

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The length of tube 320 necessary to extinguish substantially all the ions of a plasma at a given source gas flow rate may be determined experimentally or by lifetime calculations. In one embodiment, tube 320 has a length of 12 inches with a one inch inside diameter, including a one inch diameter radicals outlet 375 to produce a plasma of predominantly N^* radicals and inert nitrogen at a source gas flow rate of 300 cubic centimeters per minute at radicals outlet 375. In another embodiment, the excitation lifetime of ions is accounted for not only in plasma applicator 300 but also in inlet pipe 360 coupling plasma applicator 300 to RTP apparatus 200.

In one embodiment, energy source 450 consists of magnetron 420 and dummy load 425. Magnetron 420 generates an excitation energy, such as for example, a electromagnetic or inductively coupled frequency. The excitation energy is directed through dummy load 425 and to a wave guide to tube 320. Dummy load 425 acts, in one sense, like a check valve to allow energy flow in a direction toward plasma applicator 300 and not toward magnetron 420. Between plasma applicator 300 and tube 320 of energy source 450 is tuner 400 to redirect radiation reflected from plasma applicator 300 back toward plasma applicator 300 to increase the energy supplied to plasma applicator 300.

With reference to **Figure 3**, control signal generation logic 252 is supplied to system controller 260 in the form of, for example, software instruction logic that is a computer program stored in a computer-readable medium such as memory 238 in system controller 260. Preferably, memory 238 is a hard disk drive, but memory may also be other kinds of memory. The computer program includes, among other things, sets of

instructions that dictate the timing, gas flow rate, chamber
pressure, chamber temperature, RF power level, energy source
regulation and other parameters of a particular process. It
is to be appreciated that other computer programs such as one
stored on another memory device, including but not limited to,
a floppy disk, may also be used to operate system controller
260. The computer program is processed by system controller
260 in processor 250. The interface between a user and system
controller 260 may be implemented, for example, via a cathode
rate tube (CRT) monitor or monitor with command instruction
implemented by an interface means such as keyboard, mouse,
light-pen center, or touch screen monitor.

Figure 5 shows an illustrative block diagram of the
hierarchical control structure of control signal generation
logic 252, according to one embodiment of the invention. In a
multi-process chamber environment, for example, a user enters
a process set number and process chamber number into process
selector subroutine 473 in response to menus or screens
displayed on the CRT monitor. The process sets are
predetermined sets of process parameters necessary to carry
out specified processes, and identified by predefined set
numbers. Process selector subroutine 473 identifies (i) the
desired process chamber, and (ii) the desired set of process
parameter need to operate the process chamber for performing
the desired process. The process parameter for performing a
specific process relate to process conditions such as, for
example, process gas flow rate, temperature, reaction
pressure, cooling gas pressure, and chamber wall temperature
and are provided to the user in the form of a recipe. The
parameters specified by the process recipe are entered
utilizing the CRT monitor interface. The signals for

monitoring the process are provided by the analog input and digital input for system controller 260 and the signals for controlling the process are output on the analog output and digital output boards of system controller 460.

Process sequencer subroutine 475 shown in **Figure 5** includes, in one embodiment, program codes for accepting the identified process chamber and set of process parameters from process selector subroutine 473 and for controlling the operation of the process chamber. Multiple users can enter process set numbers and process chamber numbers, or a user can enter a multiple process set numbers and process chamber numbers, so process sequencer subroutine 475 operates to schedule the selected processes in the desired sequence. Process sequencer subroutine 475 includes a program code to perform the steps of (i) monitoring the operation of the process chamber to determine if the chambers are being used, (ii) determining what processes are being carried out in the chambers being used, and (iii) executing the desired process space on availability of the process chamber and type of process to be carried out. Conventional methods of monitoring the process chambers can be used, such as pooling. When scheduling which process is to be executed, process sequencer subroutine 475 can be designed to take into consideration the condition of the process chamber being used in comparison with the desired process condition for a selected process, or the "age" of each particular user-entered request, or any other relevant factor a system programmer desired to include for determining and scheduling priority.

Once process sequencer subroutine 475 determines which process chamber and process set combination is to be executed next, process sequencer subroutine 475 causes the execution of

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the process set by passing the particular process set parameter to chamber manager subroutine 477a-c that controls multiple processing tasks in a process chamber according to the process set determined by process sequencer subroutine 475. For example, chamber manager subroutine 477a includes program code for controlling the flow rate of process gas/plasma into process chamber 213 (through plasma applicator 300). Chamber manager subroutine 477a also controls execution of various chamber component subroutines that control the operation of chamber components necessary to carry out the selected process set. Examples of chamber component subroutines are process gas control subroutine 483, pressure control subroutine 485, and heater control subroutine 487. It is to be appreciated that other chamber control subroutine may be included depending on the process demand.

In operation, chamber manager subroutine 477a shown in **Figure 5** selectively schedules or calls the process component subroutine in accordance with the particular process set being executed. Chamber manager subroutine 477a schedules the process component subroutine similarly to the way the process sequencer subroutine 475 schedules which process chamber and process set is to be executed next. Typically, chamber manager subroutine 477a includes the steps of monitoring the various chamber components, determining which component needs to be operated based on the process parameter for the process set to be executed and causing execution of a chamber component subroutine responsive to the monitoring and determining steps.

Process gas control subroutine 483 has program code for controlling the process gas composition and flow rate. Process gas control subroutine 483 controls the open/close

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position of the safety shut-off valve, and also ramps up/down the flow controllers to obtain the desired gas flow rate. As noted above, the flow rate of process gas into plasma applicator 300 will partly determine the flow rate of radicals of a plasma delivered to substrate 100 in chamber 213. Accordingly, parameters considered in process gas control subroutine include, but are not limited to, the volume of tube 320 and the distance between the plasma generation point in tube 320 and substrate 100. Process gas control subroutine 483 is invoked by chamber manager subroutine 477a as are all chamber component subroutines, and receives from chamber manager subroutine 477a process parameters related to the desired gas flow rate. Typically, process gas control subroutine 483 operates by opening the gas supply line (by actuating flow controller 426) to begin the flow of gas into plasma applicator 300, and repeatedly (i) reading the necessary flow controller, (ii) comparing the reading to the desired flow rate received from chamber manager subroutine 477a, and (iii) adjusting the flow rate of the source gas 313 as necessary. Further, process gas control subroutine 483 includes the steps of monitoring the gas flow rate for unsafe rates and activating the safety shut-off valve when an unsafe condition is detected.

Pressure control subroutine 485 shown in **Figure 5** includes program code for controlling the pressure chamber 213 by regulating the size of the opening of the throttle valve in the exhaust system of chamber 213. The size of the opening of throttle valve is set to control the chamber pressure to the desired level in relation to the total process gas flow, size of the process chamber, and pumping set point pressure for the exhaust system. When pressure control subroutine 485 is

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invoked, the desired target pressure level is received as the parameter from chamber manager subroutine 477a. Pressure control subroutine 485 operates to measure the pressure in chamber 213 by reading one or more pressure meters connected to the chamber, compare the measured value(s) to the target pressure, obtain PID (proportional, integral, and differential) values from a stored pressure table corresponding to the target pressure, and adjust the throttle valve according to the PID value obtained from the pressure table. Alternatively, pressure control subroutine 485 can be written to open or close the throttle valve to a particular opening size to regulate chamber 213 to the desired pressure.

Heater control subroutine 487 includes program code for controlling the current to light pipe assembly 218 that is used to heat substrate 100 and chamber 213. Heater control subroutine 487 is also invoked by chamber manager subroutine 477a and receives a targeted setpoint temperature parameter. Heater control subroutine 487 measures the temperature by temperature signals delivered from fiber optic probes 271, compares the measured temperature to the set point temperature and increases or decreases the current applied to light pipe assembly 218 to obtain the set point temperature. The temperature is obtained from the measured value by looking upon the corresponding temperature in a stored conversion table or by calculating the temperature using a fourth order polynomial.

In addition to passing information to a particular chamber manager subroutine such as chamber manager subroutine 477a, process sequencer subroutine 475 causes the execution of the process set by passing the particular process set parameter to energy source manager subroutines 478a-c that

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control multiple processing steps associated with the energy source 450 determined by process sequencer subroutine 475. For example, energy source manager subroutine 478a includes program code for controlling the generation of excitation energy. Energy source manager subroutine 478a may also monitor dummy load 425 and tuner 400 to verify that any reflected energy is redirected toward plasma applicator 300 to increase the energy supply to plasma applicator 300.

The process for controlling the flow of process gas to chamber 213 can be implemented using a computer program product that is executed by system controller 260. A computer code can be written in a computer readable programming language, such as for example, 68000 assembly language C, C++, Pascal, Fortran, or others. Suitable program code is generally entered in a single file or multiple files, using a text editor, and stored or embodied in a computer usable medium, such as the memory system of a computer. As the entered code text is in a high level language, the code is compiled, and the resultant compiler code is then linked with an object code of precompiled object code, the system invokes the object code, causing the computer system to load the code in memory, from which the central processing unit (CPU) reads and executes the code to perform the task identified in the program.

A method of generating a plasma of radicals in a reaction chamber according to an embodiment of the invention is illustrated in flow chart 500 of **Figure 6**. The method of this embodiment will be described with respect to a nitrogen plasma reaction process using the remote plasma system described in **Figures 3** and **4**. Additionally, the remote plasma generation process of the invention will be described with respect to the

reaction of nitrogen radicals with SiO$_2$ layer, such as a gate oxide, on silicon wafer or substrate 100 as illustrated in **Figures 1** and **2**. Such a process might be used, for example, to create gate dielectrics having an appropriate dopant barrier layer for high performance transistor devices.

The formation of a layer of SiO$_2$ may be accomplished in the same reaction chamber as the plasma nitridation reaction of the invention. Thus, the first step according to this embodiment of the invention, as set forth in block 502, is to move wafer or substrate 100 into chamber 213. As is typical with modern cluster tools, wafer or substrate 100 will be transferred by a robotic arm from a load lock through a transfer chamber and placed onto support ring 262 located in chamber 213 as shown in **Figure 3**. Wafer or substrate 100 will generally be transferred into chamber 213 having an inert N$_2$ ambient at a transfer pressure of approximately 20 Torr. Chamber 213 is then sealed. Next, the pressure in chamber 213 is further reduced by evacuating the N$_2$ ambient through gas outlet 270. Chamber 213 is evacuated to a pressure sufficient to remove the N$_2$ ambient.

In accordance with this embodiment of the invention, silicon wafer or substrate 100 is oxidized to form a layer of SiO$_2$ by one of several known processes. For example, the oxidation may be carried out in a 100% oxygen (O$_2$) or dry O$_2$ environment at 1050°C for 50 seconds to yield an oxide layer having a thickness of 50 Å. Alternatively, the process gas may include a reactant gas mixture comprising two reacting gases: A hydrogen-containing gas and an oxygen-containing gas that can be reacted together to form steam or water vapor at temperatures between 400-1250°C. The hydrogen-containing gas is preferably hydrogen (H$_2$), or may be other hydrogen-

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containing gases such as, but not limited to, NH_3, deuterium (heavy hydrogen), and hydrocarbons such as methane (CH_4). The oxygen-containing gas is preferably O_2 gas but may be other types of oxygen-containing gases such as, but not limited to, nitrous oxide (N_2O).

It has been found that the addition of a hydrogen-containing gas to an oxygen-containing gas increases the oxidation rate on the substrate. This increased rate is particularly noted by carrying out the reaction of the hydrogen-containing gas and the oxygen-containing gas inside chamber 213 or "in situ". The gases are caused to react at or near the substrate by the heat generated by wafer or substrate 100. Accordingly, the oxygen-containing gas and the hydrogen-containing gas are preferably mixed together in chamber 213 to form the reacting gas mixture with the partial pressure of the reacting gas mixture (i.e., the combined partial pressure of the hydrogen-containing gas and the oxygen-containing gas) controlled to ensure safe reacting conditions. Such safe reacting conditions are maintained by back filling chamber 213 with process gas such that the partial pressure of the reacting gas mixture is less than the partial pressure at which spontaneous combustion of the entire volume of the desired concentration ratio of reacting gas will not produce a detonation pressure wave of a predetermined amount. The predetermined amount is the amount of pressure that chamber 213 can reliably handle without failing. An in situ method such as described using 1% H_2 gas and 99% O_2 gas for 10 seconds will produce oxide on a silicon wafer or substrate 100 having a thickness of 30 Å at a temperature of 950°C.

In addition to the in situ process described above, one oxidation process particularly useful for a gate oxide is the

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oxidation of wafer or substrate 100 by an oxygen-containing gas of N_2O. N_2O forms an acceptable oxide at 1050°C (e.g., 40 Å in 60 seconds). One advantage of using an oxygen-containing gas of N_2O is that the N_2O oxidation places approximately 0.5% of nitrogen-containing material at interface 105 of SiO_2 layer 110 and silicon substrate 100. It has been determined that the presence of nitrogen in the range of about 0.5% at the dielectric layer/silicon interface suppresses hot channel carriers, i.e., carriers moving through a transistor channel that might penetrate the gate dielectric. Thus, the presence of nitrogen in amounts around 0.5% at the interface improves the oxide integrity and reliability.

Once the desired SiO_2 layer 110 is formed, chamber 213 of RTP apparatus 200 is cooled and purged in preparation for the nitridation reaction.

Next, as set forth in block 504 of **Figure 6,** the power is set to energy source 450 and the appropriate frequency, such as for example, a microwave frequency of 2.45 gigaHertz is established. Excitation energy is then supplied to plasma applicator 300 through energy source inlet 380 in plasma applicator 300. Next, as set forth in block 506, a nitrogen source gas is introduced into plasma applicator 300 at a desired flow rate. The nitrogen process gas moves through tube 320 and past energy source inlet 380. The process gas proceeds through inlet pipe 360 into chamber 213. As the nitrogen source gas passes energy source inlet 380, the excitation energy supplied by energy source 450 converts the nitrogen source gas to nitrogen plasma in tube 320 of plasma applicator 300. The nitrogen plasma is predominantly N^* radicals, positively charged nitrogen ions, and electrons. In general, the positively charged ions have a shorter life than

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uncharged N^* radicals. It is believed that the positively charged nitrogen ions quickly seek out electrons present in the plasma and combine with the electrons in tube 320 to become charge neutral.

According to the invention, when the plasma is transferred from plasma applicator 300 to chamber 213 of RTP apparatus 200 and to the surface of the substrate, the plasma is made up primarily of charge neutral gas and plasma radicals. The plasma radicals predominantly react or interact with SiO_2 layer 110 on wafer or substrate 100 (step 512) of **Figure 6**. Any electrical bias present in chamber 213 of RTP apparatus 200 is discontinued as any electrical bias may attract positively charged nitrogen ions into chamber 213. Once the bias is eliminated and the stabilization temperature and the pre-reaction pressure are reached, chamber 213 is backfilled with the desired mixture of process gas, i.e., radicals (step 514). In the case of a nitrogen plasma, the nitrogen in the plasma available for reaction with SiO_2 layer 110 are N^* radicals.

Next, the reaction temperature of the nitridation reaction is established as set forth in block 516 of **Figure 6**. Power to lamp 219 is increased to ramp up the temperature of wafer or substrate 100 to process temperature. Wafer or substrate 100 is preferably ramped from the stabilization temperature to process temperature at a rate between 10-100°C/seconds. The preferred process temperature for the nitridation of oxide is 600°C. It is to be appreciated, however, that the nitridation can be accomplished at various temperatures, including room temperature. A comparison of the

nitridation reaction at 600°C and at room temperature (25°C)
is presented below.

As set forth in block 518, once the reaction temperature
is reached, the nitridation reaction is held for an
appropriate reaction time, in this case, an appropriate
reaction time to incorporate enough nitrogen in a gate oxide
to act as a barrier layer to gate dopants. Process time and
temperature are generally dictated by the amount of nitrogen
desired to be incorporated into the gate oxide, the thermal
budget, the purpose of the nitridation, and the amount of flow
rate of the process gases.

Next, as set forth in block 520, power to lamps 219, if
on, is reduced or turned off to reduce the temperature of
wafer or substrate 100. The temperature of wafer or substrate
100 decreases (ramps down) as fast as it is able to cool down
(at about 50°C/second). Simultaneously, N_2 purge gas is fed
into chamber 213. In general, the nitridation reaction ceases
when the radicals of the plasma are no longer present. Thus,
the nitridation reaction does not significantly continue in
the presence of the N_2 purge gas. The chamber is then
backfilled with N_2 gas to the desired transfer pressure of
approximately 20 Torr and wafer or substrate 100 is
transferred out of chamber 213 to complete the process (block
522). At this time, a new wafer or substrate may be
transferred into chamber 213 and the process set forth in flow
chart 500 repeated.

Figure 7 shows a Secondary Ion Mass Spectroscopy (SIMS)
profile of a silicon substrate containing a dielectric layer
formed by nitridation of an oxide film as described above with
reference to **Figures 1-6** and the accompanying text. The SIMS
profile of **Figure 7** illustrates the atomic profile of a

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dielectric from the surface (0 depth) to the interface of the dielectric layer and the silicon substrate. Thus, the depth represents the depth into the dielectric layer.

Figure 7 shows the profile of a nitrogen-containing dielectric material formed on a silicon wafer or substrate according to a first set of reaction conditions. In this case, the nitridation is carried out on a wafer having a SiO_2 layer. The plasma nitridation according to the invention is carried out at 600°C for 60 seconds at 1 Torr process pressure. The nitrogen plasma is produced by the addition to plasma applicator 300 of an N_2 gas at a flow rate of 300 cubic centimeters per second. Plasma applicator 300 includes a quartz tube (tube 320) of 12 inches with a one inch diameter. The N^* radicals are produced through contact with an excitation energy of a microwave frequency (2.45 gigaHertz frequency) generated at a power of approximately 1200 watts. The process gas flow rate and plasma applicator are determined and sized, respectively, so that substantially all of the positively charged ions generated by the plasma become charge neutral in the plasma applicator.

Figure 7 illustratively shows that the majority of the nitrogen-containing material present in the dielectric layer (and attributable to the nitrogen plasma reaction) is toward the surface of the dielectric layer (i.e., within 5-10 Å of the surface of the dielectric layer) and not at the dielectric layer/silicon substrate interface. **Figure 8** schematically illustrates a side view of dielectric layer 620 formed on substrate or wafer 600 utilizing a plasma nitridation process in accordance with the first set of reaction conditions. **Figure 7** shows that dielectric layer 620, having an overall thickness of approximately 46 Å, has the highest concentration

of nitrogen within 10 Å of the surface of dielectric layer 620.

A common way to measure the thickness of dielectric layer 620 is by measuring the speed of a light ray through dielectric layer 620. Since an SiO_2 dielectric material has a known refractive index (approximately 1.46), the change in the speed of the light ray through an SiO_2 dielectric layer provides a determination of the thickness of the dielectric layer.

One theory of the nitridation reaction of the invention is that N^* radicals displace oxygen atoms and form Si_3N_4 and $Si_xN_yO_z$ molecules. Si_3N_4 and $Si_xO_yN_z$ have a refractive index greater than SiO_2. Thus, the effect of a nitridation reaction according to the first set of reaction conditions of the invention will produce a change in the apparent thickness of dielectric layer 620. The change is referred to as "apparent", because, although the actual thickness may be similar before and after a nitridation reaction that results in the replacement of oxygen atoms, there will be a change in the refractive index and the change in the refractive index of the material will effect the thickness measurement. Thus, under the first set of reaction conditions, a dielectric layer thickness difference or delta of 4.24 Å was observed.

A measurement of the areal density of the nitrogen-containing material in the surface of dielectric layer 620 shows an areal density measurement of nitrogen of $4.0E14/cm^2$. An areal density measurement determines the amount of nitrogen present in the surface area of dielectric layer 620.

Figure 9 shows the SIMS profile of a nitrogen-containing dielectric layer formed on a silicon substrate or wafer with a plasma nitridation of SiO_2 under a second set of reaction

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conditions. The plasma nitridation of **Figure 8** takes place at room temperature (25°C) for 60 seconds at a process pressure of 1 Torr. The nitrogen plasma is produced by flowing a N_2 process gas of 300 cubic centimeters per second through plasma applicator 300 (12 inch length, one inch diameter) and exposing the N_2 gas to an excitation energy having a microwave frequency (2.45 gigaHertz frequency) at approximately 1200 watts power. The process gas flow rate and plasma applicator 300 are determined and sized, respectively, so that substantially all of the positively charged nitrogen ions generated by the plasma become charge neutral in plasma applicator 300. The nitridation reaction with the SiO_2 layer is carried out, in this example, for 60 seconds. **Figure 9** shows again that the plasma nitridation results in the majority of the nitrogen-containing material being present at the surface of the dielectric layer (i.e., within 10 Å of the depth of the approximately 46 Å thick dielectric layer) and not at the dielectric layer/silicon wafer interface.

Figure 10 schematically illustrates a side view of dielectric layer 720 formed on wafer 700 utilizing a plasma nitridation process in accordance with the second set of reaction conditions. A 46 Å thick dielectric layer 720 has the highest concentration of nitrogen containing material (presumably in the form of Si_3N_4 and $Si_xN_yO_z$) within 10 Å of the surface of dielectric layer 720. A refractive index light change thickness measurement shows an apparent dielectric layer thickness change of 3.44 Å from the thickness of a dielectric layer of SiO_2. An areal density measurement of nitrogen in the surface of dielectric layer 720 is $4.0E14/cm^2$.

Figures 9 and **10** demonstrate that a suitable barrier layer of nitrogen-containing material may be formed on an

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oxide in a reaction performed at room temperature. In this manner, the invention contemplates that such a barrier layer may be incorporated into an integrated circuit chip process scheme without adding to the thermal budget of the process.

The above reactions demonstrate that a nitridation of an oxide can be effectively produced with a plasma of predominantly radicals (e.g., N^*). In addition, the reactions demonstrate that a nitridation by radicals (e.g., N^*) results in an effective barrier layer being placed at the surface of the oxide and not at the interface between the oxide and the silicon wafer or substrate. In this manner, a plasma nitridation process that results in the formation of a barrier layer at the surface of the dielectric allows the incorporation of a barrier layer into, for example, a gate dielectric, that does not degrade transistor device performance. Because the reaction occurs primarily between N^* radicals and oxide (SiO_2), the nitridation (or the formation of the barrier layer) may be accomplished rapidly and, in one embodiment, without the addition of heat. Accordingly, the plasma nitridation with N^* radicals offers a manner of incorporating a barrier material on an oxide that does not require a significant thermal budget.

The above invention has been described with reference to a nitrogen plasma reaction with an oxide (SiO_2) or other material on a silicon substrate or wafer. As noted, however, the techniques described are not to be limited to nitridation of a material on a silicon substrate or wafer. Instead, the techniques may be used whenever plasma incorporation processes are practiced with a view towards efficiently incorporating the material and managing a thermal budget. In general, the

invention recognizes the effectiveness of reacting a plasma of predominantly radicals with a substrate or a material on a substrate.

A novel apparatus and method for incorporating a plasma have been described.